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Basis-set convergence in correlated calculations of molecular properties

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Abstract

An investigation of the basis-set convergence of the correlation contribution to the interaction energy of hydrogen-bonded complexes (ΔE_{corr}), to the molecular electric dipole moment ($\boldsymbol{\mu}_{corr}$), and to the relativistic two-electron Darwin term (D^{2e}_{corr}) is presented. For the correlation-consistent basis sets, the convergence of ΔE_{corr} and $\boldsymbol{\mu}_{corr}$ follows an X^{-3}-form in the cardinal number X similar to the one for the correlation energy once other significant basis-set errors than those originating from the incomplete description of the electronic Coulomb cusp have been addressed—i.e., diffuse basis functions have been included in the basis set and, in the case of ΔE_{corr}, the counterpoise correction has been applied. The convergence of D^{2e}_{corr} follows an X^{-1}-form, and the observed different rates of convergence are rationalized within a general theory framework for basis-set convergence.